product separated as fibrous yellow crystals. It was collected and vacuum dried to obtain 0.8 g of purified product; its melting point and infrared spectrum were identical with those of the crude form. *Anal.* Calcd for $MoC_8H_{16}N_2O_6S_2$ (formula wt 396.3): Mo, 24.2; C, 24.2; H, 4.1; N, 7.1; S, 16.2. Found: Mo, 23.9; C, 24.6; H, 4.2; N, 6.9; S, 16.3.

b. Prism Form.—A solution of 0.25 g of crude product in 50 ml of methanol was boiled gently for 5 min, filtered, and allowed to stand at room temperature for 2 hr. It was then refrigerated overnight to obtain 0.15 g of yellow-amber prisms contaminated with several clumps of feathery crystals; these were separated mechanically. The prism form melted at 150–151° dec. *Anal.* Found: C, 24.6; H, 4.2; N, 6.9.

Addition of a solution of 1.7 g of L-cysteine methyl ester hydrochloride in 10 ml of water to a vigorously stirred solution of 1.2 g of sodium molybdate dihydrate gave a good yield of product identical with the crude product obtained from molybdenum dioxydichloride.

Bis(ethyl cysteinato)dioxomolybdenum(VI) (6b).—This compound was prepared similarly to the methyl ester analog; crude

yield 3.3 g (77%); mp 127–128° dec. This material is very unstable in hot organic solvents; thus, heating in ethanol for as short a time as 2 min converted it to an amorphous, intractable solid. The following procedure gave purified crystalline product. To 6 ml of boiling ethanol was added 0.2 g of finely divided crude product, and the mixture was boiled for less than 1 min to effect dissolution; the solution was immediately filtered into a flask immersed in an ice bath and the filtrate was agitated while scratching the inner walls of the flask with a stirring rod. A bright yellow, crystalline solid separated and was quickly collected and vacuum dried; recovery, less than 50%. The melting point was unchanged. *Anal.* Calcd for $MoC_{10}H_{20}N_2O_6S_2$ (formula wt 424.4): Mo, 22.6; C, 28.4; H, 4.8; N, 6.6; S, 15.1. Found: Mo, 22.6; C, 28.1; H, 4.7; N, 6.3; S, 15.9.

Spectral Study of Some New Low-Symmetry Oxomolybdenum(V) Complexes[1]

BY H. E. PENCE AND J. SELBIN

The following new low-symmetry oxomolybdenum(V) complexes were synthesized and characterized by conductance, by magnetic susceptibility, and by infrared, visible–ultraviolet, and epr spectroscopy: $MoOX_3(\beta\text{-diketonate})^-$, where X = Cl or Br, and the β-diketones are benzoyltrifluoroacetone, dibenzoylmethane, hexafluoroacetylacetone, and thenoyltrifluoroacetone. Analysis of the electronic spectral data is carried out in detail and band assignments are made, somewhat securely for the ligand field spectral region and somewhat less certain for the charge-transfer and intraligand-transition spectral region.

Introduction

Until recently the interpretation of the spectra of compounds containing the oxomolybdenum(V) moiety MoO^{3+} has been predicated largely upon the treatment proposed by Gray and Hare[2] for the $MoOCl_5^{2-}$ ion. These workers presumed that the resemblance between this species and the oxovanadium(IV) entity (both of which are d^1 systems) was sufficient to permit utilization of very similar energy diagrams in both cases. This was a convenient assumption since Ballhausen and Gray[3] had previously examined oxovanadium(IV) by means of a Wolfsberg–Helmholtz type of calculation and obtained a model which seemed to explain many spectral features of that system. Although the Gray–Hare proposal has appeared to be satisfactory in many cases, some questions have arisen. This has led us to prepare and obtain spectra of several very low-symmetry oxomolybdenum(V) complexes

in order to test the validity of the Gray–Hare assignments.

Experimental Section

A. Preparation of Compounds.[4]—All reagents and solvents used were reagent grade chemicals from common commercial sources except tetraethylammonium oxopentachloromolybdate(V) and tetraethylammonium oxotetrabromomolybdate(V) monohydrate. The former material was prepared using the procedure described by Palmer[5] as appropriate for $(NH_4)_2MoOCl_5$, with the substitution of tetraethylammonium chloride for ammonium carbonate in those instructions. The bromo complex was prepared as described by Bishop;[6] an aqueous solution of tetraethylammonium bromide was added to a solution of molybdenyl hydroxide dissolved in concentrated hydrobromic acid. A yellow-brown solid formed immediately, was recovered by filtration, and then was purified by recrystallization from ethanol.

(1) $[(C_2H_5)_4N][MoOCl_3(hfa)]$.—The liquid, hexafluoroacetylacetone, was added slowly to a hot, concentrated solution of

(1) Taken in part from the Ph.D. Dissertation of H. E. Pence, Louisiana State University, 1967.
(2) H. B. Gray and C. R. Hare, *Inorg. Chem.*, **1**, 363 (1962).
(3) C. J. Ballhausen and H. B. Gray, *ibid.*, **1**, 111 (1962).

(4) The ligand ions are designated by the following abbreviations: btfa, benzoyltrifluoroacetonate ion; dbm, dibenzoylmethanate ion; hfa, hexafluoroacetylacetonate ion; ttfa, thenoyltrifluoroacetonate ion.
(5) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, Cambridge, England, 1954.
(6) A. D. Bishop, M.S. Thesis, Louisiana State University, Baton Rouge, La., 1962.

[(C₂H₅)₄N]₂[MoOCl₅] in acetonitrile. An excess of ligand (2:1 molar ratio) was used. The reaction mixture turned red almost immediately. The solvent was partially removed by warming under reduced pressure and the resulting precipitate was recovered by filtration. The crude product was recrystallized from methylene chloride and desiccated under vacuum for 42 hr. *Anal.* Calcd for [(C₂H₅)₄N][MoOCl₃(C₅HO₂F₃)]: C, 28.20; H, 3.81; Cl, 19.14; F, 20.52. Found: C, 27.96; H, 4.18; Cl, 19.25; F, 20.48.

(2) [(C₂H₅)₄N][MoOCl₃(ttfa)].—A hot solution of thenoyltrifluoroacetone dissolved in a minimum volume of acetonitrile was added to a hot acetonitrile solution of [(C₂H₅)₄N]₂[MoOCl₅] while the latter was being stirred. Two moles of ligand was used per mole of molybdenum(V). The solvent was partially evaporated and the resulting red precipitate was recovered by filtration. This product was washed several times with hot chloroform and vacuum dried. *Anal.* Calcd for [(C₂H₅)₄N][MoOCl(C₅H₄O₂F₃S)]: C, 33.73; H, 4.25; Cl, 18.67; F, 10.00; S, 5.63. Found: C, 33.51; H, 4.51; Cl, 18.78; F, 10.63; S, 5.74.

(3) [(C₂H₅)₄N][MoOCl₃(btfa)].—The procedure was the same as that described above except that the appropriate ligand was used and the crude product was washed with cold *p*-dioxane. *Anal.* Calcd for [(C₂H₅)₄N][MoOCl₃(C₁₀H₆O₂F₃)]: C, 38.35; H, 4.64; Cl, 18.87; N, 2.48. Found: C, 38.36; H, 4.88; Cl, 17.95; N, 2.70.

(4) [(C₂H₅)₄N][MoOCl₃(dbm)].—A similar procedure was employed using acetone as the solvent, dibenzoylmethane as the ligand, and hot tetrahydrofuran as a wash solution. *Anal.* Calcd for [(C₂H₅)₄N][MoOCl₃(C₁₅H₁₁O₂)]: C, 48.21; H, 5.46; Cl, 18.60; N, 2.45. Found: C, 48.02; H, 5.63; Cl, 18.29; N, 2.67.

(5) [(C₂H₅)₄N][MoOBr₃(dbm)].—The ligand, dibenzoylmethane, was dissolved in a small amount of acetonitrile and added to a concentrated solution of [(C₂H₅)₄N][MoOBr₄H₂O] in the solvent. After partial evaporation a black, crystalline compound formed which was washed several times with hot tetrahydrofuran. The product, a reddish black, crystalline solid was vacuum dried for several days. *Anal.* Calcd for [(C₂H₅)₄N][MoOBr₃(C₁₅H₁₁O₃)]: C, 39.17; H, 4.43; Br, 34.00. Found: C, 39.08; H, 4.79; Br, 34.15.

Efforts to prepare other similar complexes using various β-diketones were unsuccessful. Although in some cases the reaction mixture changed from green to red or orange, it was not possible to isolate any pure products.

B. Analyses.—The analyses for carbon and hydrogen were performed by the departmental analyst; other elements were determined by Micro-Tech Laboratories, Inc., Skokie, Ill.

C. Spectral Measurements.—Infrared spectra of Nujol mulls containing the compounds were observed in the range 4000–650 cm⁻¹ by means of a Beckman Model IR-7 recording spectrophotometer, and a Beckman Model IR-10 instrument was used to observe the 650–300-cm⁻¹ region. The frequencies of the Mo≡O and Mo—O (chelate) stretching vibrations were assigned for each compound and are listed in Table I.

TABLE I

CHARACTERIZATION DATA FOR THE OXOMOLYBDENUM(V) COMPLEXES

Compound	Mo≡O[a] str, cm⁻¹	Mo—O (chelate)[a] str, cm⁻¹	μ_{eff}, BM	Molar conductivity,[b] cm² ohm⁻¹	g_{av}[c]
[(C₂H₅)₄N][MoOCl₃(hfa)]	976	499	1.75	210	1.947
[(C₂H₅)₄N][MoOCl₃(ttfa)]	965	512	1.87	150	...
[(C₂H₅)₄N][MoOCl₃(btfa)]	966	515	1.77	150	...
[(C₂H₅)₄N][MoOCl₃(dbm)]	956	547	1.63	174	1.945
[(C₂H₅)₄N][MoOBr₃(dbm)]	955	550	1.69	193	1.982

[a] Nujol mull samples. [b] For various concentrations between 10⁻³ and 10⁻⁴ *M* in acetonitrile. Previous workers have reported for 1:1 electrolytes in this solvent conductances of 112–154 (L. V. Interrante, *Inorg. Chem.*, **7**, 943 (1968)), and 168–208 (R. S. Drago and K. F. Purcell in "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press, New York, N. Y., 1965, pp 211–251). [c] For solutions in degassed acetone having concentrations of 10⁻⁴ *M*.

Near-infrared, visible, and ultraviolet spectra were measured with a Cary Model 14 spectrophotometer. Each compound was examined in solutions of acetonitrile and dichloromethane at room temperature as well as in Nujol mulls at liquid nitrogen temperatures. The observed frequencies and suggested assignments are found in Table II. Because the spectra were so similar in the two different solvents, only the results for the acetonitrile solutions are given. Where the shift of a band in dichloromethane is considered important, the magnitude of the effect is indicated in the discussion.

Electron paramagnetic resonance spectra of some of the complexes were ascertained using a Model JES-3BX, X-band spectrophotometer produced by The Japan Electron Optics Laboratory, Co., Ltd. The values of g_{av} are given in Table I. The

TABLE II

VISIBLE AND ULTRAVIOLET SPECTRAL DATA FOR THE MoOX₃L²⁻ ANIONS[a]

X = Br, L = dbm	X = Cl, L = dbm	X = Cl, L = btfa	X = Cl, L = ttfa	X = Cl, L = hfa	Assignments[a]
[12.9][b]				[12.9]	
14.1 (41)	13.6 (30)	13.8 (32)	13.7 (35)	14.2 (30)	$d_{x^2-y^2} \to d_{xz}, d_{yz}$
18.2 (550)	18.4 (50)	19.2 (300)	18.9 (300)	18.9 (80)	$d_{x^2-y^2} \to d_{xy}$
	19.7 (50)	20.5 (200)	20.1 (400)	20.3 (80)	
[21.8]	22.2 (420)	[24.1]	[23.8]	[23.7]	
22.7 (6000)	23.7 (410)	25.1 (4000)	24.9 (20,000)	25.4 (2600)	$\pi \to d_{x^2-y^2}$
		[26.1]			
[27.3]			[28.2]	[28.5]	
29.5 (50,000)	29.2 (11,000)	[29.9]	29.1 (39,000)	32.2 (11,000)	$\pi_3 \to \pi_4$[c]
			31.7 (36,000)		
	32.8 (15,000)	33.6 (40,000)			
35.6	35.5				
				[39.7]	
				[40.5]	
				42.7 (12,000)	
40 (40,000)	[39.4]	[38.2]			

[a] All frequencies are in kilokaiser units (kK); 1 kK = 1000 cm⁻¹. [b] Extinction coefficients are in parentheses; shoulder bands are enclosed in brackets. [c] The transition $d_{x^2-y^2} \to d_{z^2}$ is presumed to occur at high frequencies (>30 kK) and to be covered by more intense charge-transfer and intraligand transitions.

spectrum of a manganese(II) compound was used to calibrate the instrument.

D. Other Physical Measurements.—Conductivity measurements were made at 25° on freshly prepared 10^{-3} to 10^{-4} M acetonitrile solutions which had been allowed to attain thermal equilibrium. Values were determined with an Industrial Instruments Model RC16 conductivity bridge. The values of the molar conductances are also listed in Table I.

Magnetic susceptibilities of the finely powdered samples were evaluated by the Gouy method and the magnetic moments were calculated using diamagnetic corrections listed by Selwood.[7] Cobalt tetrakis(thiocyanato)mercurate(II) and tris(ethylenediamine)nickel(II) thiosulfate were the calibrants for the procedure and the results are shown in Table I.

Results, Assignments, and Discussion

A comparison of the ir data given in Table I reveals an inverse relationship between the Mo≡O multiple bond stretching frequency and the Mo—O single bond stretching frequency which is logically consistent with the thesis that the strengthening of some bonds to a central atom often will weaken certain others; this appears to be the case, for example, with oxovanadium-(IV) complexes.[8] Also it is interesting to note that changing the bidentate oxygen-donor ligand has a more pronounced effect on the metal–oxygen frequencies than changing the remaining three ligands from chloride to bromide.

The tendency of oxomolybdenum(V) complexes to form dimers and higher polymeric species has been noted by many investigators and the evidence for this behavior has been reviewed by Mitchell.[9] The monomeric nature of the new compounds reported here has been verified in solution and in the solid state on the basis of magnetic susceptibilities and epr spectra.

The high degree of covalency between the oxo group and the molydenum(V) ion is reflected in a substantial reduction of the spin–orbit coupling constant and as a result the magnetic moments approximate the spin-only values, as is seen in Table I. If the complexes are polynuclear, the moments would be expected to be much smaller or the compounds might be diamagnetic. (However this is not necessarily so, as there are polynuclear complexes (*e.g.*, certain Cu(II) complexes) which do not have reduced moments.) Since the g_{av} values obtained for solutions of the complexes (see Table I) are very similar to those reported[8] for the corresponding oxopentahalo complexes, which are known to be monomeric, there is evidently no appreciable polymerization in solution.

The coordinate system chosen is shown in Figure 1. In the absence of exact structural information it has been assumed that the β-diketone ligand lies completely in the plane perpendicular to the metal–oxo group multiple bond, rather than having one point of attachment in the axial position. Thus we expect that the stronger ligand oxygen (from β-diketone) will not prefer a site *trans* to the multiply bonded oxygen, and furthermore all β-diketone complexes of VO^{2+}
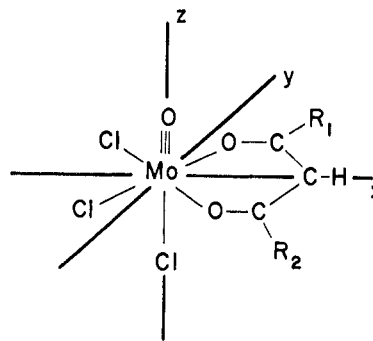

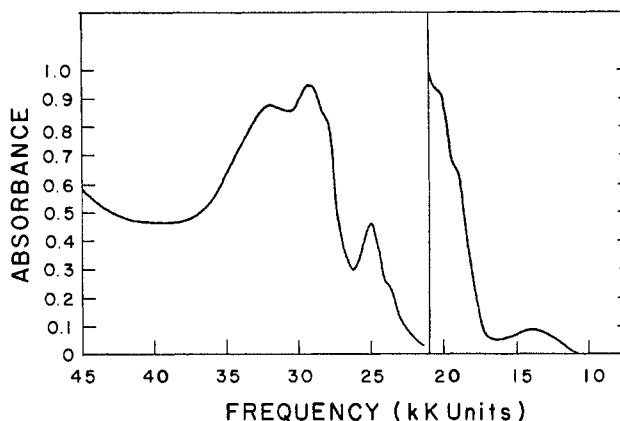Figure 1.—Coordinate system used in C_s symmetry for the complexes $MoOCl_3(\beta\text{-diketonate})^-$.

Figure 2.—Electronic spectrum of $[(C_2H_5)_4N][MoOCl_3(ttfa)]$ in acetonitrile solution. Concentrations are 2.34×10^{-4} M in the 10–21-kK region and 1.9×10^{-5} M in the 21–45-kK region.

whose structures are known[8] have the ligand atoms in the equatorial plane. Additionally we find no evidence for an equilibrium mixture of the two forms, since the electronic spectra are the same in Nujol mulls as in two different solvents. In any case the discussion of the electronic spectra is independent of the structure that is assumed. Under these circumstances the ions will belong to point group C_s if the β-diketone is symmetrical (*i.e.*, R_1 is identical with R_2) and C_1 for the symmetrical ligands.

The visible and ultraviolet spectral data of the new compounds in acetonitrile solution are summarized in Table II. Extinction coefficients are listed for many of the bands which are distinct; however, there was considerable overlapping of the various band systems, especially in the ultraviolet region, and so they do not provide a completely dependable measure of the actual intensities. Some of the results are obviously questionable, such as the absorption observed at 24.9 kK in the spectrum of the $MoOCl_3(ttfa)^-$ ion. This intensity is completely inconsistent with the similar bands in the other compounds, no doubt owing to just such overlapping. A sample spectrum, that for $[(C_2H_5)_4N][MoOCl_3(ttfa)]$, is shown in Figure 2.

In each compound a relatively low-intensity, broad band is found at a frequency of approximately 14 kK. The frequency, intensity, and broadness of this transi-

(7) P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1956.

(8) J. Selbin, *Chem. Rev.*, **65**, 153 (1965); *Coord. Chem. Rev.*, **1**, 293 (1966).

(9) P. C. H. Mitchell, *Quart. Rev.* (London), **20**, 103 (1966).

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tion indicate that it is almost surely analogous to that assigned as $d_{xy} \rightarrow (d_{xz}, d_{yz})$ by Gray and Hare.[2] In the coordinate system used here the transition would be designated as $d_{x^2-y^2} \rightarrow (d_{xz}, d_{yz})$.[10] As has been frequently pointed out,[2,6,9] the persistence of a band of this type at the same frequency in so many different oxomolybdenum(V) complexes and its insensitivity to the ligands present in addition to the oxo group seem to make this the only reasonable assignment. The symmetry of the compounds under discussion is so low that the degeneracy of the d levels is expected to be completely removed,[2,3,8] but there is no definite evidence of this in the spectral observations. The band does develop a clearly discernible shoulder in Nujol mulls at liquid nitrogen temperatures, but it is not possible to determine if this is really the expected splitting or simply an especially prominent vibrational band. The vibrational structure of this absorption is clearly visible at low temperatures and the spacing is approximately 1000 cm^{-1}, which is consistent with the proposed assignment.

It is observed that all but one of the compounds have a pair of moderate-intensity absorptions at about 20 kK. The lone exception, $[(C_2H_5)_4N][MoOBr_3(dbm)]$, has a single peak at 18.2 kK. Although the intensity of these bands is higher than that usually expected for d–d transitions, this is not unreasonable for very low-symmetry compounds and so this is presumed to be the $d_{x^2-y^2} \rightarrow d_{xy}$ transition. This assignment is also in agreement with the Gray–Hare proposal for $(NH_4)_2MoOCl_5$. At liquid nitrogen temperatures a second band appears at 19.5 kK for the bromo complex and the pair of bands in each of the other compounds becomes more distinct. This is consistent with the assumption that the bands in question are due to a d–d absorption split by vibrational interaction. The energy for this transition is equal to the $10Dq$ value of these compounds.

The third d–d band, $d_{x^2-y^2} \rightarrow d_{z^2}$, has not been assigned and is thought to lie at much higher frequencies where it is covered by the intense charge-transfer and intraligand bands. Wentworth and Piper[11] have put forth very convincing arguments that the analogous band in the spectrum of the $MoOCl_5^{2-}$ anion must lie at high frequencies in order to produce reasonable values for the parameters Ds and Dt. The same type of reasoning would apparently be valid in the case of the compounds under discussion here.

All of these ligand field band assignments are in agreement with the Gray–Hare proposals for the similar compound $(NH_4)_2MoOCl_5$, if the difference in coordinate system is considered. The situation is less clear when the charge-transfer spectra are examined.

Gray and Hare suggested that the three intense bands in the ultraviolet spectrum of the $MoOCl_5^{2-}$ ion were charge-transfer transitions due to the excita-

tion of an electron from a bonding e_π molecular orbital to the antibonding levels which consist primarily of the metal d orbitals. They neglect completely the possibility of metal–chlorine π bonding and presume that π orbitals from the oxo group are the predominant component of the e_π level.

Allen, et al.,[12] compared the spectra of $MoOBr_5^{2-}$ and $WOCl_5^{2-}$ with the $MoOCl_5^{2-}$ spectrum and found the results difficult to explain if metal–halogen π bonding were completely ignored. The position of the charge-transfer bands for these compounds was strongly shifted relative to the frequency of apparently analogous bands in the spectrum of the oxopentachloromolybdate (V) ion. In all three cases the frequency of the first d–d transition, in which an electron is excited from a b_2 energy level, consisting primarily of the metal d orbitals, to an e_π level formed in part from the oxygen π orbitals, is found at about the same frequency, 14 kK. If the energy difference between these two levels is relatively unchanged, it is difficult to explain a large shift in the bonding level composed of the oxo group π orbitals. Further, Horner and Tyree[13] have noted a great similarity in the charge-transfer bands of MX_6^- and MOX_5^{2-} (where M = Nb, Mo, or W and X = Cl or Br). All of these workers concur in suggesting that the Gray–Hare scheme be modified by including a substantial contribution from the halogen π orbitals in the bonding e_π level.

A third approach to the problem has been proposed by Kon and Sharpless,[14] who believe that the highest energy filled bonding molecular orbital for the oxopentahalomolybdate(V) complexes is a σ level and that the transition of an electron from this level to molecular orbitals consisting primarily of the metal d orbitals is the best explanation of the charge-transfer bands observed in these complexes. They point out that the metal–oxygen bond is very important and that the strength of the metal–halogen bonds in these complexes must be correspondingly weak; perhaps so weak that exciting an electron from a σ-bonding halogen orbital will require less energy than the transition from the π levels. This suggestion is consistent with the observations of Allen, et al.,[12] and also seems to provide an explanation for the unusual g values reported by Kon and Sharpless[14] and others,[15] but it does not explain the similarity in the charge-transfer spectra of the MX_6^- and MOX_5^{2-} ions observed by Tyree and Horner.[13] If Kon and Sharpless are correct, the absence of the oxo group should drop the σ-bonding level to lower energy and cause a significant change in the spectra.

Each of the new compounds under consideration

(10) Wherever it appears that no ambiguity might result, the common practice will be followed of using the metal d orbital to represent the molecular orbital of which it is a principal component.

(11) R. A. D. Wentworth and T. S. Piper, *J. Chem. Phys.*, **41**, 3884 (1964).

(12) E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Chem. Soc.*, 4649 (1963).

(13) S. M. Horner and S. Y. Tyree, *Inorg. Nucl. Chem. Letters*, **1**, 43 (1965).

(14) H. Kon and N. E. Sharpless, *J. Phys. Chem.*, **70**, 105 (1966).

(15) K. DeArmond, B. B. Garrett, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 1019 (1965).

has a pair of moderate-intensity bands in the region 20–26 kK which are probably charge transfer in origin. The similarity in frequency as well as the magnitude of the splitting between the two bands leads us to suggest that they are all similar in origin and the splitting is caused by a vibrational progression. If these bands represent excitation of an electron from the oxo group to the metal, it is difficult to understand why the substitution of the β-diketone for the halo groups should cause a shift of several kilokaisers, especially when the frequency of the first d–d transition has remained much the same as that observed in the $MoOCl_5{}^{2-}$ ion. On this basis it is judged unlikely that this particular set of absorption bands involves any substantial contribution from the oxo group. Further, the similarity in the band frequency when $MoOCl_3(dbm)^-$ and $MoOBr_3(dbm)^-$ are compared seems to require that this transition also be independent of any contribution from either the σ or π levels of the halogen ligands. On the basis of the exclusion of other possibilities, it seems most likely that this is a charge-transfer transition involving the β-diketone and the lowest energy metal d orbital.

To determine if the ligand orbitals are σ or π levels the far-infrared spectra of the compounds were examined to ascertain if the ligand-to-metal bonds seemed unusually weak. Comparing these metal–oxygen (chelate) stretching frequencies (see Table I) with those reported for compounds not containing an oxo group[18] seems to show no substantial decrease in frequency such as might be expected if the bonds were weak.

The $d_{x^2-y^2}$ orbital is thought to lie between the π₃ and π₄ β-diketone levels because if this half-filled orbital were higher in energy than the empty π₄ level, the electron would tend to drop into the lower-energy, empty orbital, thereby oxidizing the metal. Similarly, the molybdenum would tend to be reduced if the half-filled metal orbital were lower in energy than π₃. In summary it is considered most likely that the pair of bands at 20–26 kK are ligand-to-metal charge-transfer transitions, originating in the π₃ level of the β-diketone.

Recently Ogden and Selbin[17] reported the observation of the singlet–triplet, intraligand absorption at 20–25 kK for several β-diketone complexes of oxovanadium(IV). No bands were found in the spectra under discussion which might fit this assignment. If such absorptions were present in these compounds, the more intense charge-transfer bands discussed previously would obscure them.

The region beyond 26 kK is complicated by the presence of many bands some of which could not be completely resolved. One intense absorption which will surely appear in this region is the π₃ → π₄ intraligand transition. Several investigators[17,18] have re-

ported this transition between 30 and 40 kK for the free ligands and various β-diketone complexes.

Solutions of the free ligands in acetonitrile have broad bands corresponding to this assignment at the following values: Hdbm, 29.5 kK; Hbtfa, 30.6, Httfa 31.1; and Hhfa 32.7. The energy for the π₃ → π₄ free ligand transition thus appears to decrease in the order Hhfa > Httfa > Hbtfa > Hdbm, and the band frequency in the complexes should decrease in a similar fashion.

In two cases, $MoOBr_3(dbm)^-$ and $MoOCl_3(hfa)^-$, only one intense band is found in the appropriate spectral region and the assignment is straightforward. The transition in question should not be especially sensitive to the substituents attached to the metal ion and so a similar band at 29.4 kK in the $MoOCl_3(dbm)^-$ spectrum almost surely has the same origin.

The π₃ → π₄ band is predicted to have its highest frequency in the $MoOCl_3(hfa)^-$ ion spectrum (32.2 kK) and so it seems unlikely that the band at 33.6 kK in the $MoOCl_3(btfa)^-$ spectrum corresponds to this transition. For that reason the shoulder at 29.9 kK is identified as the π₃ → π₄ absorption in this complex ion. Since in each of the above cases the band assigned as π₃ → π₄ is at a slightly lower frequency than the similar band in the free ligand spectrum, it is reasonable to suppose that a similar shift will occur for the $MoOCl_3(ttfa)^-$ anion and this is the basis for assigning the 29.1-kK absorption as the π₃ → π₄ excitation.

Comparison of the spectra in acetonitrile and dichloromethane solutions gives support to the above assignments. In a less polar solvent, such as dichloromethane, the frequency of the π₃ → π₄ band is expected to be shifted to higher frequencies relative to its position in the strongly polar acetonitrile. A small shift to higher energies was observed for each assigned band. The other bands which might be considered in three of the compounds all showed a substantial shift toward lower frequency in the less polar solvent.

The π₃ → d_{xy} transition frequency may be estimated by the equation

$$(E_{\pi_3 \to d_{xy}}) = (E_{\pi_3 \to d_{x^2-y^2}}) + (E_{d_{x^2-y^2} \to d_{xy}}) - (R_{d_{x^2-y^2}})$$

where E's are the energies observed for the indicated transitions (see Table II) and R is the repulsion energy involved in placing a second electron in the $d_{x^2-y^2}$ orbital (as in the π₃ → $d_{x^2-y^2}$ transition). It is not necessary to include a repulsion term for the π₃ level since it would appear on both sides of the equality sign and cancel. Assuming 6 kK as a reasonable repulsion energy, R, the bands are predicted to fall between 30 and 35 kK and by adjusting the R value, fair agreement can be obtained with a number of the observed bands. However, definite assignments are not attempted on this basis because other charge-transfer transitions involving the halogen and perhaps even the oxo π orbitals may fall in this same region.

The substantial change in the spectra of these compounds when compared with the oxopentahalomolyb-

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date(V) complex discussed by Gray and Hare seems to be incompatible with their supposition that only the oxo group makes a substantial contribution to the ground state of the charge-transfer transitions. A choice between placing the σ ligand levels above or below the π levels is more difficult. The portion of the spectrum which would provide the best information with regard to this question is unfortunately obscured by the intense intraligand transitions characteristic of the β-diketone ligands.

No firm assignments have been attempted for the bands beyond 35 kK. The absorption at about 40 kK in the compounds containing phenyl groups is probably the $\pi \rightarrow \pi^*$ transition of the benzene ring, but the spin-allowed $\pi_3 \rightarrow \pi_5$ and $\pi_2 \rightarrow \pi_4$ intraligand transitions may also be found in this region.

CONTRIBUTION FROM THE FACULTY OF ENGINEERING,
UNIVERSITY OF TOKYO, BUNKYO-KU, TOKYO, JAPAN

Stereochemical Studies of Metal Chelates. III.[1] Preparation and Stereochemistry of Cobalt(III) Complexes with C-Substituted Triethylenetetramines at the Central Ethylenediamine Bridge

BY MASAFUMI GOTO, MASAHIKO SABURI, AND SADAO YOSHIKAWA

The preparation of dichloro- and dinitrocobalt(III) complexes of optically active C-substituted triethylenetetramine at the central ethylenediamine bridge is described. The stereoselective formation of the *cis-β* isomer was observed and the stereochemical details are discussed in terms of the conformation of each chelate ring as well as the configurations of the secondary nitrogen atoms. The rearrangement of *cis-β*-dichloro complexes to *trans* isomers is also reported.

In the past few years, some interesting reactions of cobalt(III) complexes of triethylenetetramine (trien) and its derivatives have been reported, *i.e.*, hydrolysis of the N-terminal peptide bond,[2] formation of a dipeptide ester from amino acid esters,[3,4] and an asymmetric synthesis of α-alanine.[5] Concurrently, studies on the stereochemistry of the cobalt(III) complexes containing trien have been in rapid progress. It was pointed out formerly that three geometrical isomers may exist in diacido trien complexes, namely, *cis-α*, *cis-β*, and *trans* as shown in Figure 1.[6] Sargeson and Searle have succeeded in resolving several *cis-α* and *cis-β* isomers of $Co(trien)X_2^{n+}$[7] and have assigned their absolute configuration on the basis of circular dichroism and rotatory dispersion studies.[8] These authors also indicated that the *trans*-Co(trien)Cl₂⁺ ion derived from optically active *cis-β* isomer is asymmetric.[9]

Furthermore, the possibility that two different isomers may exist in *cis-β* form was recognized assuming different types of the two asymmetric secondary nitrogen atoms.

In a previous paper,[10] it was reported that L,L-3,8-dimethyltriethylenetetramine (L,L-3,8-dimetrien) was coordinated stereospecifically to the cobalt(III) ion, yielding the optically active *trans*-Co(L,L-3,8-dimetrien)Cl₂⁺ ion, and that racemic 5-methyltriethylenetetramine (5-metrien) was found to give stereoselectively the *cis-β*-Co(*dl*-5-metrien)Cl₂⁺ ion. These results indicate that alkyl groups substituted at the carbon atoms adjacent to the secondary nitrogen atom in trien control the geometrical isomer form of dichloro complexes. However, L,L-2,9-dimethyltriethylenetetramine (L,L-2,9-dimetrien),[11] as well as unsubstituted trien, was observed to give the *cis-α* isomer under similar preparative conditions. In order to investigate the effect of position of the substituted group in trien, new optically active trien derivatives containing alkyl groups at the central ethylenediamine bridge have been synthesized; these are shown in Figure 2, and the dichloro- and dinitrocobalt(III) complexes containing these ligands have been prepared. Consequently, it was concluded that these complexes yielded only the *cis-β* isomer and the chirality of the ligands controls stereospecifically the absolute configuration of the complexes. Furthermore, the conformation of each chelate ring in the geometrical isomers will be discussed in detail from the examination of stereomodels.

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